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Amber McGivern

Montana Tech of the University of Montana

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Geochemistry and Stable Isotopes of Surface Water and Groundwater in the Continental Pit in Butte, Montana, USA

Amber L. McGivern

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Department of Geological Engineering
Montana Tech of the University of Montana
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Research Committee:

Dr. Chris Gammons (Chair)

Dr. Glenn Shaw (Montana Tech, Dept. of Geological Engineering)

Dr. Gary Icopini (Montana Bureau of Mines and Geology)

Abstract

The Continental porphyry Cu-Mo mine, located 2 km east of the famous Berkeley Pit lake of Butte, Montana, contains two small lakes that vary in size depending on mining activity. In contrast to the acidic Berkeley Pit lake, the Continental Pit waters have near-neutral pH and relatively low metal concentrations. The main reason is geological: whereas the Berkeley Pit mined highly-altered granite rich in pyrite with no neutralizing potential, the Continental Pit is mining weakly-altered granite with lower pyrite concentrations and up to 1-2% hydrothermal calcite.

The purpose of this study was to gather and interpret information that bears on the chemistry of surface water and groundwater in the active Continental Pit. Pre-existing chemistry data from sampling of the Continental Pit were compiled from the Montana Bureau of Mines and Geology and Montana Department of Environmental Quality records. In addition, in March of 2013, new water samples were collected from the mine's main dewatering well, the Sarsfield well, and a nearby acidic seep (Pavilion Seep) and analyzed for trace metals and several stable isotopes, including δD and $\delta^{18}O$ of water, $\delta^{13}C$ of dissolved inorganic carbon, and $\delta^{34}S$ of dissolved sulfate. In December 2013, several soil samples were collected from the shore of the frozen pit lake and surrounding area. The soil samples were analyzed using X-ray diffraction to determine mineral content.

Based on Visual Minteq modeling, water in the Continental Pit lake is near equilibrium with a number of carbonate, sulfate, and molybdate minerals, including calcite, dolomite, rhodochrosite ($MnCO_3$), brochantite ($CuSO_4 \cdot 3Cu(OH)_2$), malachite ($Cu_2CO_3(OH)_2$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$), gypsum, and powellite ($CaMoO_4$). The fact that these minerals are close to equilibrium suggests that they are present on the weathered mine walls and/or in the sediment of the surface water ponds. X-Ray Diffraction (XRD) analysis of the pond "beach" sample failed to show any discrete metal-bearing phases. One of the soil samples collected higher in the mine, near an area of active weathering of chalcocite-rich ore, contained over 50% chalcantite ($CuSO_4 \cdot 5H_2O$). This water-soluble copper salt is easily dissolved in water, and is probably a major source of copper to the pond and underlying groundwater system. However, concentrations of copper in the latter are probably controlled by other, less-soluble minerals, such as brochantite or malachite.

Although the acidity of the Pavilion Seep is high (~ 11 meq/L), the flow is much less than the Sarsfield Well at the current time. Thus, the pH, major and minor element chemistry in the Continental Pit lakes are buffered by calcite and other carbonate minerals. For the Continental Pit waters to become acidic, the influx of acidic seepage (e.g., Pavilion Seep) would need to increase substantially over its present volume.

Key words: neutral mine drainage, trace metals, pit lake, geochemistry, mineral solubility

Introduction

Just east of the famous Berkeley Pit lake in Butte, Montana (Davis and Ashenberg, 1989), there is a lesser known active open pit mine, the Continental Pit. The Continental Pit contains a large but low-grade Cu-Mo porphyry deposit (Czehura, 2006). Two surface water bodies exist on the property, here called the North Pond and the South Pond (Fig. 1). Presently, the elevations of these lakes are maintained at a low level by the Sarsfield pumping well, located near the north shore of the North Pond. Pumping ceased in 2001-2003 after the mine temporarily shut down in 2000 due to unfavorable economics. Dewatering resumed in 2003 when the mine reopened, and continues to the present day, at a typical rate of 800 to 1200 liters per minute (S. Czehura, pers. comm. March 2013).



Figure 1. Google Earth image showing the location of the North and South Ponds in the Continental Pit, with the nearby Berkeley Pit lake for comparison. The Pavilion Seep (not shown) is located on the southeast wall of the Continental Pit. Image taken July 16, 2002.

During the mine-closure period of 2000-2003, samples of groundwater from the Sarsfield Well and/or samples of surface water from the North Pond (Fig. 2A) were collected monthly by the Montana Bureau of Mines and Geology (MBMG). Since 2006, the active mine has been collecting water samples twice a year from several locations on their property, including the North and South Ponds, the Sarsfield Well (sampled instead of the North Pond when the latter is dry or frozen), and the Pavilion Seep. The water quality results are sent to the Montana Department of Environmental Quality (MDEQ), and are publically available upon request. The Pavilion Seep is a relatively small volume of acidic groundwater that enters the Continental Pit from a bench on the southeast

highwall. At the time of this writing, Pavilion Seep water is collected and pumped to a site outside of the pit where it is mixed with Sarsfield Well water and used in the mill.

Because the active mining company intends to continue open-pit mining for decades, no formal plans for closure of the Continental Pit exist. The final closure scenario may well *not* include a pit lake. Nonetheless, it is interesting to look at the data in hand to predict the water quality of a hypothetical lake formed from flooding of the Continental Pit, and to compare this result to the nearby Berkeley Pit lake (Fig. 2B).

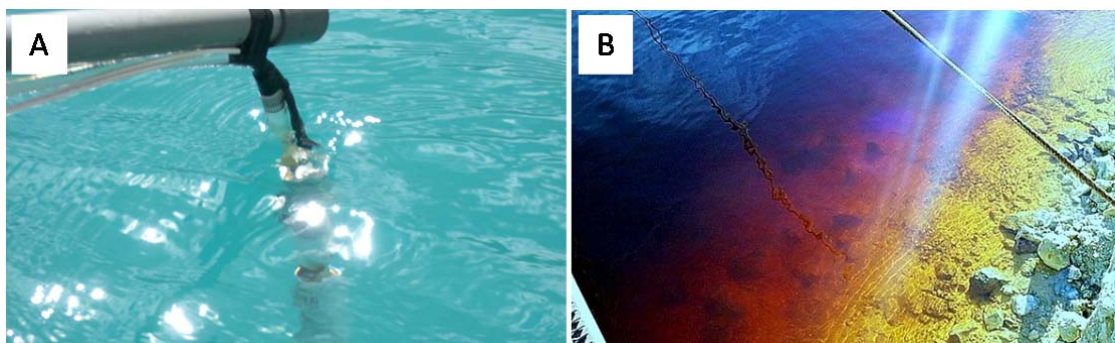


Figure 2. Close-up photographs comparing the appearance of water in the North Pond of the Continental Pit (left, with a submersible pump) and the Berkeley Pit lake (right). Photos courtesy of Nick Tucci, MBMG.

Berkeley Pit Background

The Berkeley Pit began filling with water in 1983, when mining operations ceased, and shortly thereafter became a Superfund site (Gammons and Duaime, 2006; Metesh, 2006). The pit lake is a part of the Clark Fork Basin Superfund Complex, the largest Superfund complex in the United States (Moore and Luoma, 1990; US-EPA, 1994). Its location at the headwaters of Silver Bow Creek, which eventually flows into the Clark Fork River, makes it an important water body to monitor. The geochemistry of the Berkeley Pit lake has been investigated by many agencies and academic groups for decades (Davis and Ashenberg, 1989; Pellicori et al., 2005; Gammons and Duaime, 2006; Gammons and Tucci, 2013). Samples are currently collected biannually by the MBMG, and water quality results posted on the internet at the Bureau's Groundwater Information Center site (GWIC, 2013). Based on the US-EPA's Record of Decision (US-EPA, 1994), a water treatment plant will need to begin treating Berkeley Pit water before the elevation of the lake reaches 5410' above sea level, the so-called "critical level". Currently, the critical level is projected to be reached sometime near 2023 (Pitwatch, 2014). With the exception of the bottom of the active Continental Pit, the critical level of 5410' represents the lowest elevation in the Butte Summit Valley. The

groundwater divide that separates the pit lake and surrounding flooded mine workings from Silver Bow Creek is shown in Figure 3.

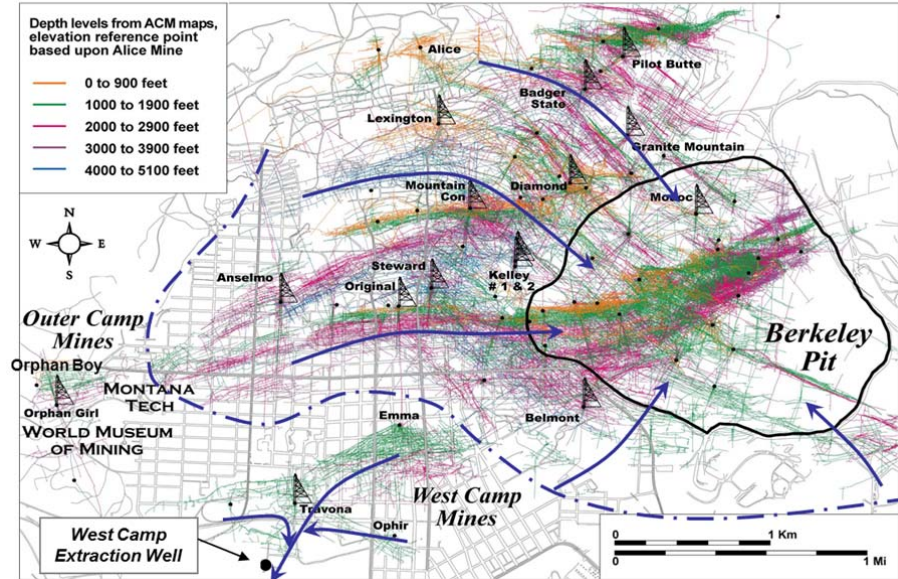


Figure 3. Groundwater flow map with underground workings of various levels shown. The dashed and dotted line represents a groundwater divide (Duaime et al., 2004; Gammons, et al., 2009).

Geology

The deposits in Butte are Cu-Mo porphyry style deposits cut by rich Cu-Pb-Zn-Mn-Ag lode veins (Houston and Dilles, 2013). These deposits are hosted in Butte Quartz Monzonite, part of the Boulder Batholith, which is approximately 76 million years old (Rusk et al., 2008). The Berkeley Pit was mined for chalcocite-rich supergene ores and zones of deeper, closely-spaced veins that were left behind by the underground mines (Czehura, 2006). The main ore minerals of the Continental Pit are chalcopyrite and molybdenite (Czehura, 2006). This deposit is located in a portion of the Pittsmont Dome that has been uplifted by the Continental Fault (Fig. 4). The Continental Fault is a normal fault with over 1000 m of displacement (Rusk et al., 2008).

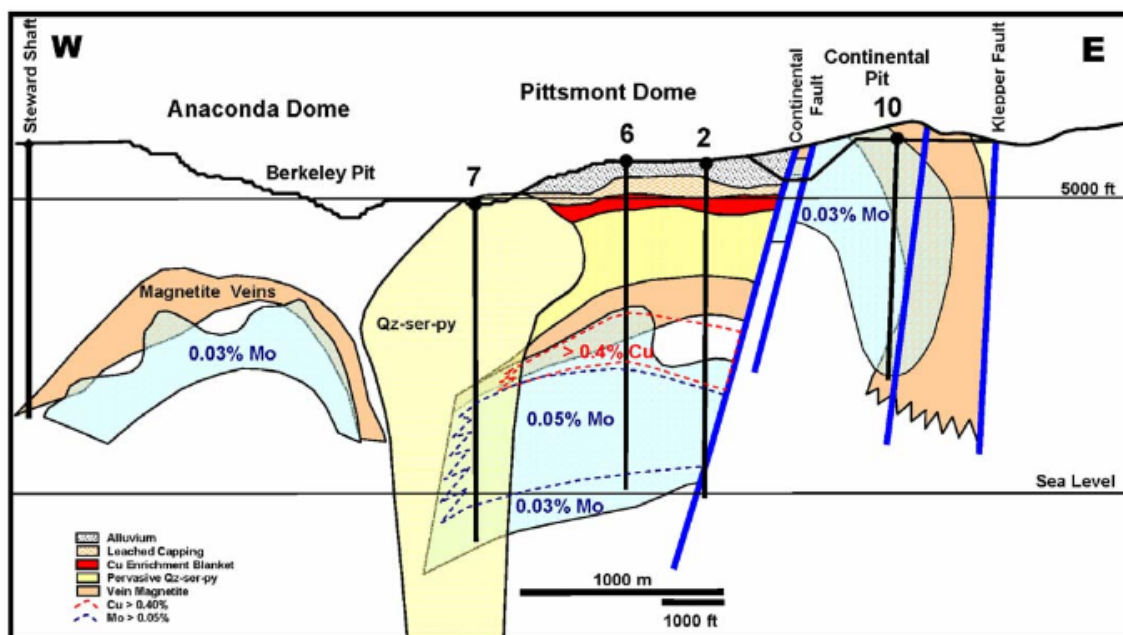


Figure 4. Geologic cross section of the Berkeley and Continental Pits, showing location of the Anaconda and Pittsmond Domes (Czehura, 2006).

Methods

Water chemistry data for the North Pond from 2001 to 2003 were downloaded from the MBMG's Groundwater Information Center website (GWIC, 2013). In June of 2003, shortly before dewatering resumed, a vertical profile of field parameters in the North Pond was collected by MBMG from a boat, and water samples were taken at near-surface and at a depth of 11 m. Additional data for the North Pond, the South Pond, and the Pavilion Seep collected between 2006 and 2012 were provided by MDEQ. All of the water quality analyses were conducted by certified labs following strict quality assurance protocols. In March 2013, the author sampled the discharges from the Sarsfield Well and the Pavilion Seep. Samples were submitted for chemical analysis, as well as determination of $\delta^{18}\text{O}$ and δD of water, $\delta^{34}\text{S}$ of dissolved sulfate, and $\delta^{13}\text{C}$ of dissolved inorganic carbon. In December 2013, soil samples were collected from the shores of the North Pond and bottom of the Continental Pit. These samples, which contained secondary copper salts, were ground to a fine powder using a mortar and pestle and isopropyl alcohol and then analyzed by X-Ray Diffraction (XRD) at the Dept. of Metallurgical Engineering, Montana Tech.

Data for each chemical analysis of the North Pond between 2001 and 2003 ($n = 17$) were input into the program Visual Minteq, v. 3.0 (a recent adaptation of the original MINTEQA2 program of Allison et al., 1991), and saturation indices (S.I.) were estimated for a number of minerals and amorphous solid phases. In this paper, the S.I. values for

each solid were adjusted to one metal ion per formula unit. For example, amongst the common secondary Cu minerals, the S.I. value for malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) was divided by two and the S.I. value for azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) was divided by three. This was done so that S.I. values could be more equally compared between a set of minerals that contain a common element of interest. For modeling purposes, dissolved Cu and Mn were assumed to be in the +2 valence, and Mo and U were assumed to be +6. Fe was assumed to be +2 in the Sarsfield Well and Pavilion Seep, and +3 in the Continental Pit lake waters. These redox assignments are consistent with the presence of > 5 mg/L dissolved oxygen throughout the water column of the north lake in June 2003 (see below).

Results

Water quality results from 2013 sampling of the Sarsfield Well were relatively similar to past data; most of the major ions were present in quantities slightly lower than in past samples (Table 1). Cu, Mn, and Zn concentrations were slightly higher than past averages, while the concentration of Fe was significantly higher than the average concentration during mine closure and moderately higher than the average concentration during mining activity (7.47 mg/L compared to 0.05 and 4.0 mg/L respectively).

While sampling the Sarsfield Well at its discharge point, the pH was measured at 5.83. The sample sat in the open for a few minutes and during this time the pH rose to 6.8. This was likely due to degassing of dissolved CO_2 . By inputting the field pH of 5.83, the alkalinity, and the temperature into Visual Minteq, a CO_2 partial pressure of 0.16 atm was obtained. This is much higher than the equilibrium partial pressure of CO_2 in air (around 0.0003 atm at the elevation of Butte), and explains why $\text{CO}_2(\text{g})$ would rapidly diffuse out of the sample after pumping to the surface. For the purpose of calculating saturation indices (below), the pH of 5.83 was used.

The chemical compositions of the North and South Ponds in the Continental Pit are very similar (see Table 1). Both water bodies have a pH near 7, with a significant amount of bicarbonate alkalinity (> 100 mg/L as CaCO_3). The concentrations of most metals of concern, such as Cu and Zn, are quite low when compared to the Berkeley Pit lake, but are nonetheless well above regulatory standards for surface water. However, it is emphasized that these standards are not relevant as long as the mine is in operation.

Table 1. Chemical composition of selected water bodies of interest in the vicinity of the Continental Pit.
All solute concentrations are in mg/L

Location	pH	SC ¹	Ca	Mg	Na	K	SO ₄ ²⁻	Cl ⁻	F ⁻	HCO ₃ ⁻	NO ₃ -N	PO ₄ -P
Data from this study												
Sarsfield Well	5.83	1940	396	32	36	5.3	1100	9.0	2.8	146	<0.01	<0.02
Pavilion Seep	2.87	1853	249	73	28	6.0	1200	n/a	n/a	< 1	n/a	n/a
Previous Results												
CP-N surface ²	7.34	2050	433	37	38	10	1241	9.1	3.3	146	1.3	<0.5
CP-N surface ³	7.05	n/a	502	43	36	8	1310	8.9	4.2	123	0.6	0.04
CP-N 11 m ⁴	6.55	2140	477	46	41	11	1440	8.6	4.3	92	1.7	<0.5
CP-S surface ⁵	7.33	1860	397	38	32	6.1	1070	8.9	4.1	115	0.23	0.08
Pavilion ⁶	3.31	2360	225	86	24	4.6	2060	5.3	4.7	< 1	0.57	0.14
BPit surface ⁷	2.75	7340	475	534	74	9.6	8170	<50	30	< 1	<5	<5
BPit 210 m ⁷	2.53	8160	442	515	74	7.6	9090	<50	30	< 1	<5	<5
	Al	As	Cd	Cu	Fe	Mn	Mo	Ni	Si	Sr	U	Zn
Data from this study												
Sarsfield Well	0.44	0.001	0.01	0.66	7.74	3.78	0.45	0.018	10.5	2.61	0.08	3.89
Pavilion Seep	14.8	<.015	0.21	33.7	14.2	15	n/a	0.09	22	1.24	n/a	20.5
Previous results												
CP-N surface ²	0.98	0.001	0.05	0.43	0.05	3.1	0.69	0.031	5.5	4.07	0.29	3.14
CP-N surface ³	1.01	0.005	0.04	1.61	4.0	5.5	n/a	0.043	9.3	2.94	n/a	6.46
CP-N 11 m ⁴	0.18	<.005	0.17	3.71	0.04	5.5	0.55	0.039	5.4	5.27	0.22	8.92
CP-S surface ⁵	0.24	0.003	0.06	1.05	0.23	8.6	n/a	0.047	8.7	1.75	n/a	6.76
Pavilion ⁶	41	0.02	0.43	58.6	76.7	22	n/a	0.15	28	0.66	n/a	46.2
BPit surface ⁷	275	0.135	2.26	79	564	261	<0.02	2.4	38	1.55	1.97	627
BPit 210 m ⁷	268	0.097	2.27	153	1007	248	<0.02	1.6	36	1.43	1.45	638

¹Specific conductance in $\mu\text{S}/\text{cm}$; n/a = not analyzed

²Continental Pit North Pond, average of 17 samples collected in 2001-2003 (GWIC, 2013)

³Continental Pit North Pond or Sarsfield pumping well, average of 11 samples collected in 2005-2012 (MDEQ, 2013)

⁴Lake sample collected at depth of 11 m (GWIC, 2013)

⁵Continental Pit South Pond, average of 10 samples collected between 2005 and 2012 (MDEQ, 2013)

⁶Pavilion Seep, average of 11 samples collected between 2005 and 2012 (MDEQ, 2013)

⁷Berkeley Pit lake samples collected on Nov. 6, 2007 (GWIC, 2013).

Unlike some pit lakes with neutral or alkaline pH, the concentration of arsenic in both of the Continental lakes is not particularly high ($< 10 \mu\text{g}/\text{L}$). This is not due to a lack of As in the ore body, since the Butte deposits are locally rich in the Cu-As-sulfide minerals enargite and tennantite (Meyer et al., 1968). It is possible that As is being adsorbed onto secondary Fe-oxy-hydroxide minerals on weathered bedrock surfaces. In contrast to the Berkeley Pit, which has undetectable quantities of dissolved Mo (Table 1), concentrations of Mo in the North Pond are elevated (in the 0.5 to 0.7 mg/L range). This difference is geological, as the Berkeley deposit produced no Mo, whereas molybdenite is an important ore mineral at the Continental deposit (Czehura, 2006). Between 2006 and 2012, the Pavilion seep had an average pH of 3.31, and concentrations of dissolved

metals and metalloids were much higher than in the North and South ponds, but still considerably lower than the Berkeley Pit lake (Table 1). Compared to historical data provided by the MDEQ, the Pavilion Seep sample collected in this study had lower concentrations of most solutes with the exception of Ca, Na, and K. Very little is known about the hydrology of the Pavilion Seep, and it is possible that water being pumped from that location may be a mixture of acid mine drainage and background groundwater with the relative proportion changing at different times of the year.

Figure 5 summarizes long-term trends in the concentrations of Cd, Cu and Zn in the North Pond and/or Sarsfield Well between 2001 and 2013. During the period of mine closure (2001-2003), concentrations of these metals steadily increased. The North Pond was seasonally stratified during this time (Fig. 5), with a chemocline situated at a depth of 4.2 m in June 2003. A single water sample collected at 11 m depth had slightly lower pH and significantly higher concentrations of Cd, Cu and Zn compared to a near-surface sample (Table 1). Dissolved oxygen concentrations were > 5 mg/L at all depths, which is in contrast to the Berkeley Pit lake, which typically has undetectable DO concentrations below the top 1-3 m (Pellicori et al., 2005). Although the monitoring data became more scattered after resumption of mining operations in 2003, average values for most water quality parameters in the North Pond from 2001-2003 are similar to those from 2006-2013, suggesting that water quality trends have been fairly stable in the last decade.

As shown in Figure 6, vertical changes in physical parameters in the North Pond in June, 2003 were relatively small. A weak chemocline existed at a depth of 4.2 m, with slightly higher SC and lower pH below this layer. Temperature remained between 8 and 9°C at all depths. Dissolved oxygen concentrations were > 9 mg/L above the chemocline, but dropped below 6 mg/L towards the bottom of the lake (Fig. 6).

Based on the computed saturation indices (Fig. 7), water in the North Pond in 2001-2003 was close to equilibrium with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and fluorite (CaF_2), as well as a number of carbonate minerals, including calcite, dolomite, smithsonite (ZnCO_3), hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), and rhodochrosite (MnCO_3). On average, the lake waters were undersaturated with otavite (CdCO_3). It is possible that Cd resides as an impurity in calcite or another carbonate phase. A large number of Cu(II) minerals were also near equilibrium, including malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), langite ($\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$), and possibly atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$). The Sarsfield Well sample collected in March 2013 had similar

results for the saturation indices of most minerals except carbonate minerals, which were consistently under saturated relative to the North Pond samples (Fig. 7). The main reason for this difference is that the Sarsfield Well has a lower pH when freshly pumped due to a high partial pressure of dissolved CO_2 . If the saturation index calculations are repeated using the pH value of 6.8 obtained after the sample had sat in the open for several minutes, the S.I. values for carbonate minerals are more similar to the historical values for the North Pond.

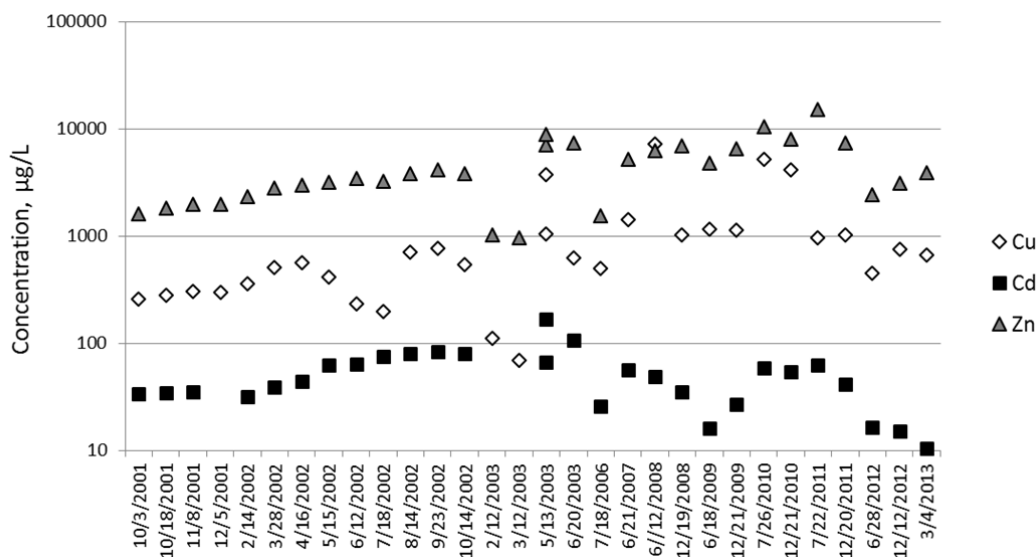


Figure 5. Concentrations of Cu, Cd, and Zn in the North Pond from 2001 through 2003 (GWIC, 2013), from 2006 through 2012 (MDEQ, 2013) and 2013 (this study). Some of the latter data are from the Sarsfield Well. The elevated concentrations from May 13, 2003 were from a sample collected at a depth of 11 meters in the North Pond.

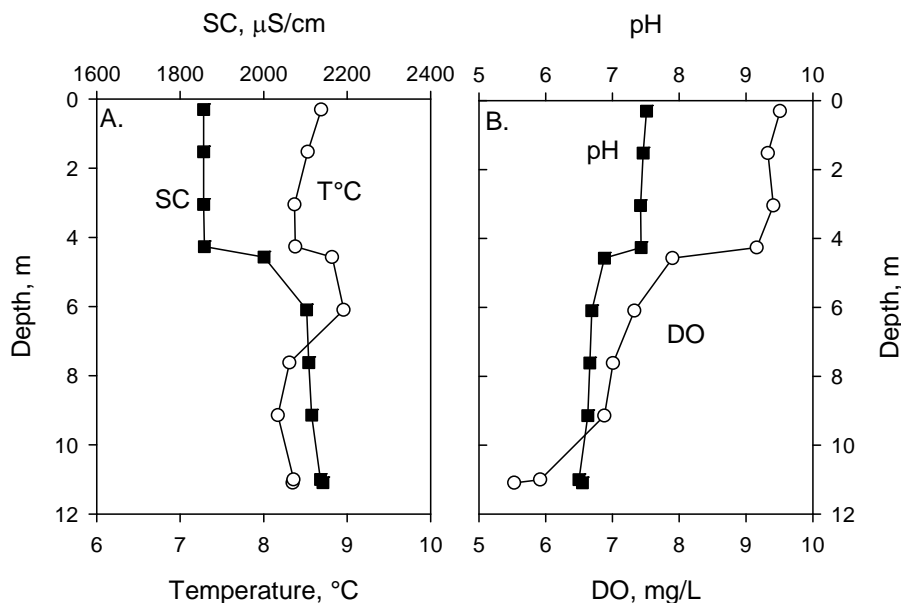


Figure 6. Vertical profiles in water temperature, specific conductance (SC), pH, and dissolved oxygen (DO) for the North Pond of the Continental Pit, collected on June 12, 2003.

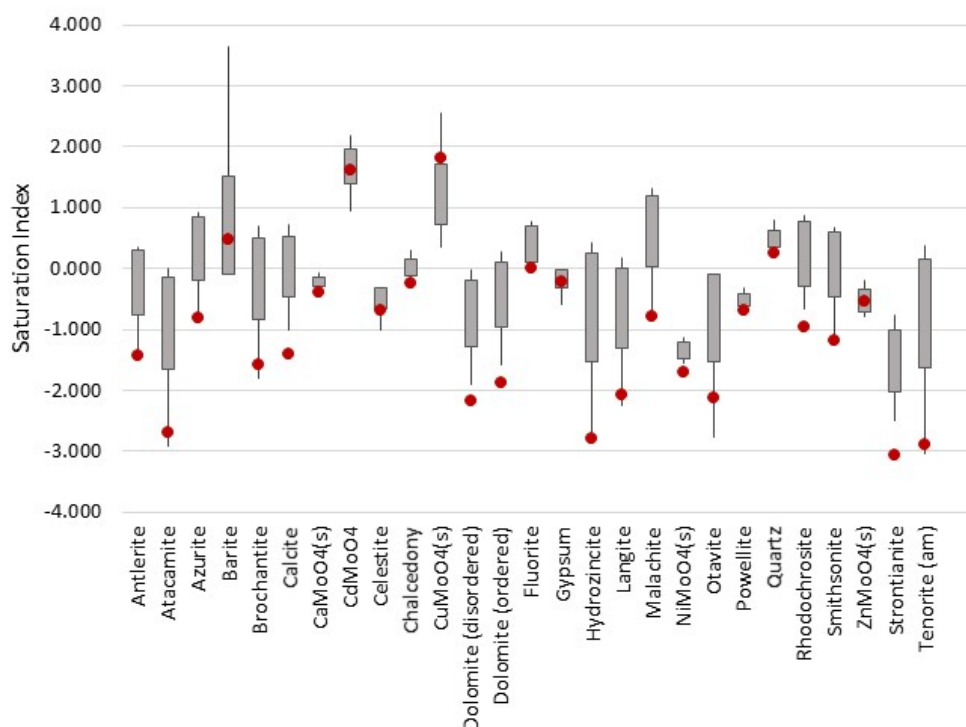


Figure 7. Saturation indices of various minerals based on 17 chemical analyses of the North Pond of the Continental Pit. Rectangles represent one standard deviation. Lines extend to maximum and minimum values. Red points represent data from the Sarsfield Well collected in 2013.

Both the North and South Ponds have a distinctive greenish blue color (Fig. 1, Fig. 2A), which could be partly caused by precipitation of one or more of these sparingly soluble secondary copper minerals. Samples of precipitates from around the North Pond and on the floor and wall of the Continental Pit were obtained and analyzed using X-ray diffraction. At the time of sampling, the North Pond was frozen and samples from below the water line could not be obtained. A sample of a blue mineral obtained from a chalcocite-rich part of the ore on the side of the Continental Pit was determined by XRD analysis to be chalcantite ($\text{Cu}_5\text{SO}_4 \cdot 5\text{H}_2\text{O}$). It is unlikely that chalcantite is stable in the pond water itself, since it is too soluble (saturation indices are strongly negative, and are not shown in Fig. 7). After rain events, the chalcantite on the ground surface probably dissolves and is flushed into the groundwater and/or the mine ponds. Much of this copper probably re-precipitates as other, less soluble Cu minerals, such as brochantite or malachite. However, the existence of these less soluble minerals in the pond could not be tested in this study.

It is significant that metal concentrations in the North Pond appear to be controlled by mineral solubility limits, as this means that the concentrations of elements such as Cd, Cu, Mn, and Zn cannot increase without a simultaneous decrease in pH and/or

bicarbonate concentration. Amongst the various silica polymorphs, the lake waters were closest to equilibrium with chalcedony (micro-crystalline quartz). Finally, it is interesting that the lake waters were found to be near equilibrium or supersaturated with several molybdate minerals, including CaMoO_4 , CdMoO_4 , CuMoO_4 , and ZnMoO_4 . This is not surprising considering the abundance of molybdenite, an important ore mineral, in the deposit.

Acidity and Alkalinity

In 2013, the Sarsfield Well had an alkalinity of 146 mg/L CaCO_3 , which is equivalent to 2.39 meq/L of alkalinity. The acidity of the Pavilion Seep collected on the same day was calculated to be 5.19 meq/L, as shown in the table below. These calculations assume that all dissolved Fe in the Pavilion Seep was ferrous (Fe^{2+}), and that each mole of dissolved Al contains 3 moles of metal acidity and that each mole of dissolved Fe, Cu or Zn contains 2 moles of metal acidity. Using averages of data from MDEQ, the acidity of the Pavilion Seep is 11.03 meq/L, significantly higher than the alkalinity of the Sarsfield Well. Although the flow from the Pavilion Seep is small relative to the flow from the Sarsfield Well, it is noteworthy that the acidity of the Pavilion water is 2 to 5 times higher than the alkalinity of the dewatering well. If the volume of acidic water in the Continental Pit were to increase in the future, the total acidity could possibly exceed the acid-buffering capacity of the non-acidic groundwater and surface water on the mine property. This possibility cannot be evaluated further with the data of this study alone.

Table 2. Pavilion Seep acidity calculations. Concentration (mmol/L) = concentration (mg/L)/gram formula weight of element, except H^+ , which was calculated using the average pH of the Pavilion Seep. meq/L obtained by dividing the concentration (mmol/L) by the charge of the element.

Element	Average Concentration (mg/L)	2013 Concentration (mg/L)	Average Concentration (mmol/L)	2013 Concentration (mmol/L)	Average Acidity (meq/L)	2013 Acidity (meq/L)
Fe^{2+}	77	14.2	1.38	0.25	2.76	0.51
Al^{3+}	41	14.8	1.52	0.55	4.56	1.65
Cu^{2+}	59	33.7	0.93	0.53	1.86	1.06
Zn^{2+}	46	20.5	0.70	0.31	1.41	0.63
H^+	-	-	0.45	1.35	0.45	1.35
Total Acidity =					11.03	5.19

Water, Sulfur, and Carbon Isotopes

Results for stable isotopic analysis of water, dissolved inorganic carbon (DIC), and sulfate are in Table 3.

TABLE 3. Results from isotopic analysis of samples from the Sarsfield Well and the Pavilion Seep.

Location	$\delta^{13}\text{C-DIC}$	$\delta^{34}\text{S-Sulfate}$	$\delta^{18}\text{O-H}_2\text{O}$	$\delta\text{D-H}_2\text{O}$
Sarsfield Well	-6.8	2.5	-17.8	-141
Pavilion Seep	-	3.0	-17.7	-137.5

The isotopic compositions of $\delta^{18}\text{O}$ and δD in the Sarsfield Well and Pavilion Seep waters are similar to water in the flooded mine shafts of Butte, and plot near the intersection of the Butte Meteoric Water Line (MWL) and Local Evaporation Line (LEL) (see Fig. 8). As discussed by Gammons et al. (2006), the intersection of the MWL and LEL most likely represents average recharge waters in Butte that have not been affected by evaporation. In contrast, the Berkeley Pit lake and the Yankee Doodle tailings pond were moderately to highly evaporated when the samples plotted in Figure 8 were collected (see Pellicori et al., 2005). The further out along the LEL a given sample plots, the more water was lost to evaporation.

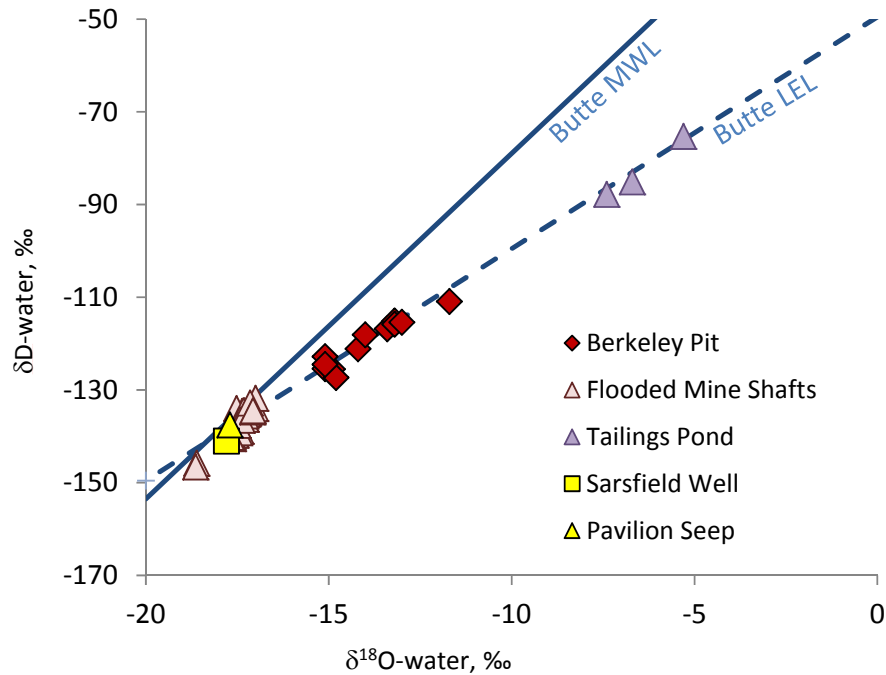


Figure 8. Isotopic data for samples collected in this study (Sarsfield Well, Pavilion Seep) plotted against the Butte Meteoric Water Line and Local Evaporation Line. Data for the Berkeley Pit, the flooded mine shafts, and the tailings pond are from Gammons et al. (2006) and Gammons et al. (2009)

The fact that the water in the Sarsfield Well is similar to that of groundwater in the flooded mine shafts and not to the Berkeley Pit lake or tailings pond water is evidence that neither the Berkeley Pit lake nor the tailings pond is leaking to any significant degree into the Continental Pit at this time. The water-isotope data clearly show that the water from the Sarsfield Well (and from the Pavilion Seep) is similar to average recharge waters in Butte, and has not been evaporated. Monitoring the stable isotope composition of water in the Sarsfield Well over time could be a low-cost method to see if this situation changes in the future if, for example, the active mine expands towards the Berkeley Pit.

The isotopic composition of sulfate in the Butte underground mine waters and the Berkeley Pit lake is the result of three processes: oxidation of pyrite and other sulfides, dissolution of sulfate minerals, and bacterial sulfate reduction (Gammons et al., 2009). In Figure 9, S-isotopic compositions of dissolved H_2S are much more depleted in $\delta^{34}\text{S}$ compared to sulfate in the same mine waters due to the large fractionation factor associated with bacterial sulfate reduction (Seal, 2003; Gammons et al., 2009). Dissolved sulfate in the Sarsfield Well and Pavilion Seep has S-isotopic compositions similar to that of pyrite in the Butte deposit (Field et al., 2005). It is also similar to sulfate in the Berkeley Pit lake (Pellicori et al., 2005). The Continental Pit shows no evidence of bacterial sulfate reduction, as has been seen in the flooded mine shafts of the West Camp and Outer Camp (Gammons et al., 2009), so it is likely that the S-isotopic compositions are from oxidation of pyrite.

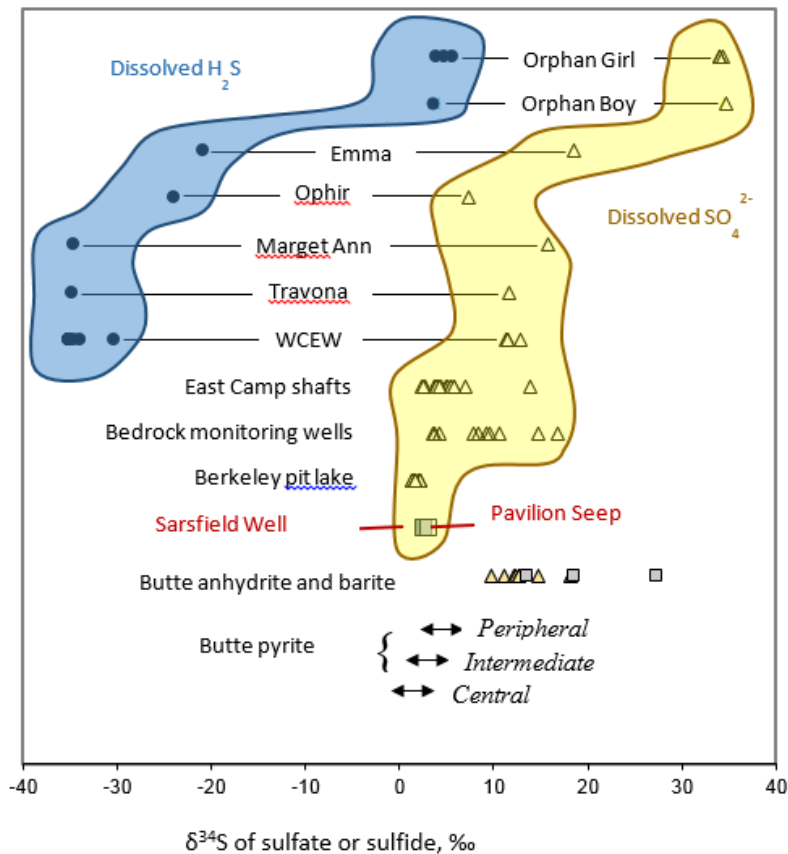


Figure 9. Sulfur isotope composition of dissolved sulfate in the Sarsfield Well and Pavilion Seep, compared to other mine waters from Butte. Data for sulfate and sulfide from the West Camp Extraction Well (WCEW) and the other mine shafts are summarized in Gammons et al. (2009). Data from the Berkeley Pit are from Pellicori et al. (2005). Data for Butte pyrite, anhydrite, and barite are from Field et al. (2005).

Dissolved inorganic carbon (DIC) in the Sarsfield Well is a mix of dissolved CO_2 and HCO_3^- ion that is isotopically heavier than other mine waters in the Butte district (see Fig. 10). In most of the flooded mine shafts of Butte, DIC has a C-isotope composition that is close to equilibrium with hydrothermal rhodochrosite in the Main Stage veins, based on data for the latter given in Garlick and Epstein (1966). DIC in the Outer Camp workings (e.g., Orphan Girl and Orphan Boy) has much lighter $\delta^{13}\text{C}$ -DIC, due to inputs of light CO_2 from bacterial sulfate reduction (Gammons et al., 2009). The DIC in the Sarsfield Well shows no evidence of input of biogenic CO_2 , and probably came from dissolution of calcite in the Continental ore body. Calcite in the Continental Pit occurs as late veins and disseminations in altered granite, and comprises as much as 1% or more of the rock volume (Newbrough and Gammons, 2002; Lamsma, 2012). Although it was not possible to analyze any of this calcite for C-isotopes in this study, data in Garlick and Epstein (1966) show that hydrothermal calcite in the Butte District is about 3‰ heavier in $\delta^{13}\text{C}$ than rhodochrosite. So, the fact that the Sarsfield Well has heavier DIC could

partly be explained by the abundance of calcite and scarcity of rhodochrosite in the Continental deposit. Some isotopic enrichment of DIC may also have been caused by loss of CO₂ during sampling or preparation of the Sarsfield Well water for DIC isotope analysis. As shown by Clark and Fritz (1997), dissolved CO₂ is about 10‰ lighter in $\delta^{13}\text{C}$ compared to HCO₃⁻ ion. So, loss of CO₂ during sampling would have caused the $\delta^{13}\text{C}$ of the remaining DIC to become heavier.

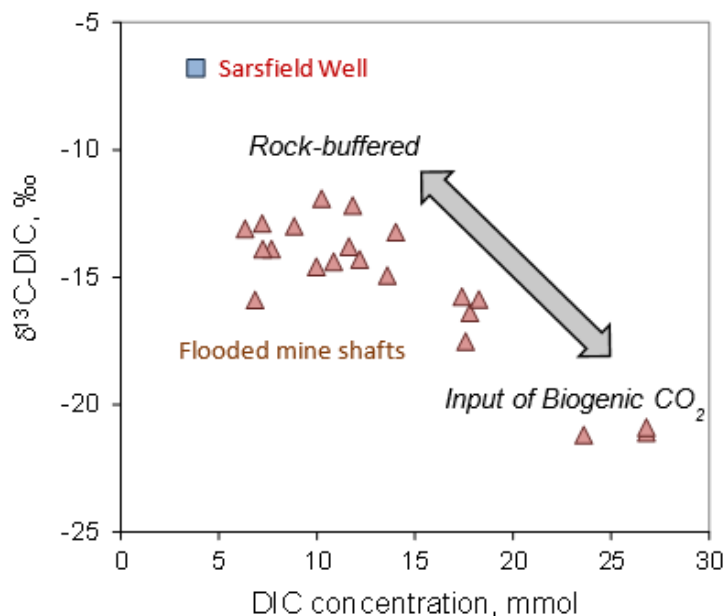


Figure 10. Carbon isotope composition of dissolved inorganic carbon in the Sarsfield Well compared to other mine waters from Butte (mine shaft data from Gammons et al., 2009).

Discussion

The data presented above show a stark contrast between the highly acidic and metal-rich Berkeley Pit lake and the nearby Continental Pit lakes which have neutral pH and relatively low metal concentrations. The main reason for this difference is geological. The two open pit mines are separated by the Continental Fault (Fig. 1), a large normal fault with > 1 km of vertical displacement (Czehura, 2006; Rusk et al., 2008), down-dropped to the west. The Berkeley deposit is rich in pyrite (> 5 wt %) with highly altered granitic bedrock (all feldspar and mafic minerals converted to muscovite and/or clay + quartz) that has no acid-neutralizing potential. In contrast, the Continental deposit, which represents a deeper and more peripheral mineral assemblage within the Butte District, contains weakly-altered granite wall rock (fresh feldspars with abundant primary and secondary biotite) with lower pyrite content (1 to 2 wt %) and a small but

significant quantity of hydrothermal calcite. The latter occurs as thin veins and disseminations throughout the ore body (Newbrough and Gammons, 2002; Lamsma 2012). Thin sections in Figure 11, taken during the study of Newbrough and Gammons (2002), compare the mineralogy of the pits. In addition, whereas the Berkeley Pit is surrounded and underlain by 1000's of km of underground mine workings (Duaiame et al., 2004; Gammons et al., 2009), very few underground workings extended into the Continental Pit area. Thus, the hydrology of groundwater flow is dominated by open or backfilled/collapsed voids in the vicinity of the Berkeley Pit, as opposed to fractured bedrock in the vicinity of the Continental Pit.

Newbrough and Gammons (2002) characterized rock samples from the Berkeley and Continental Pits by conducting static acid-base accounting (ABA) tests. Three samples were collected from the Continental Pit; two from the east side of the Continental Fault that are weakly potassic/phyllic altered, and one from the west side of the fault that represented phyllic alteration like many of the samples from the Berkeley Pit. The results of the tests are in Figure 12. The 3:1 and 1:1 slopes represent neutralization potential ratios (NPR), or the ratio of acid neutralizing potential to acid generating potential (NP/AP). It was determined that while both sample sets from each pit had acid generating potential, the Berkeley Pit samples were far more likely to generate acid. The sample from the far west side of the Continental Pit behaved like the Berkeley Pit samples, as it also showed high AP and almost no NP.

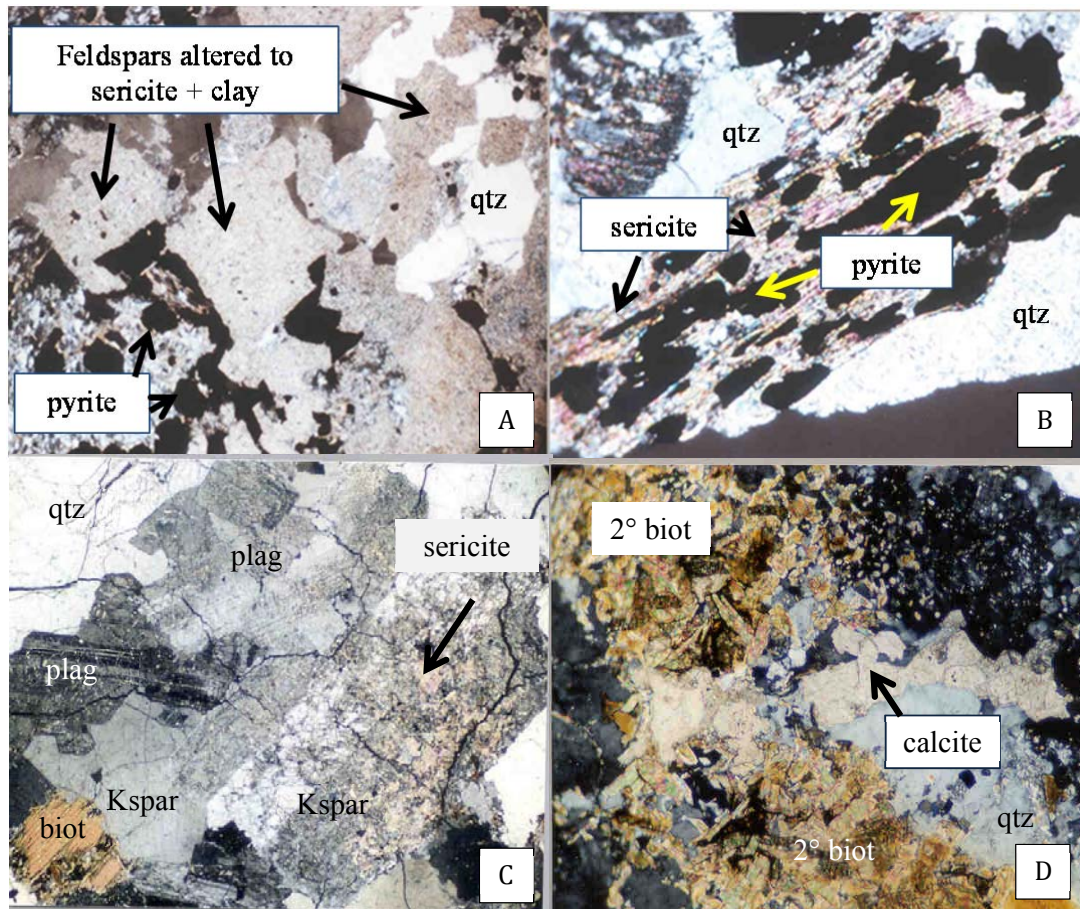


Figure 11. Thin sections from the Berkeley Pit (A and B) and Continental Pit (C and D). qtz = quartz, biot = biotite, Kspar = potassium feldspar, plag = plagioclase feldspar.

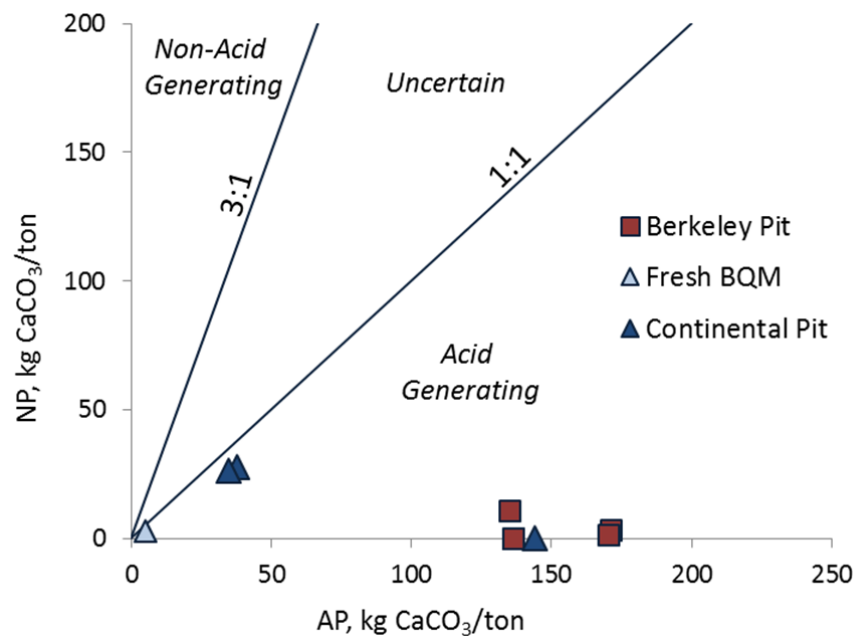


Figure 12. Results of ABA testing of samples from the Berkeley Pit and Continental Pit. BQM is Butte Quartz Monzonite. From Newbrough and Gammons (2002).

Newbrough and Gammons (2002) also used long-term humidity cell tests to compare leachate from crushed bedrock exposed in the Berkeley and Continental Pits, and found very similar water chemistry results to the data presented in this paper. However, Newbrough and Gammons observed that calcite was being depleted from the crushed Continental Pit samples faster than pyrite was being oxidized. Extrapolation of these results suggested that the Continental Pit leachates could become acidic at a future time, when the neutralizing potential was completely depleted. Due to the small number of samples in the Newbrough and Gammons study, and the inherent difficulty of scaling humidity cell tests to field settings, it is difficult to say if or when the small ponds in the Continental Pit might become acidic. The Pavilion Seep shows that some acidic drainage already exists in the Continental Pit. Although the volume of this acidic water is presently much less than the pH-neutral, alkaline water that resides in the ponds or that is being pumped from the Sarsfield Well, the acidity of the acid drainage is 2 to 5 times greater than the alkalinity of the non-acidic waters. Over time, the relative volumes of acidic and non-acidic waters could change with continued weathering of the ore body.

Conclusions and Recommendations

The Continental Pit contains two small lakes that have near neutral pH and relatively low metal concentrations compared to the Berkeley Pit lake, which is highly acidic. Mining activity is expected to continue for decades, and closure plans for the Continental Pit may not include a pit lake. Based on Visual Minteq modeling, the existing ponds in the Continental Pit are close to equilibrium saturation with a number of carbonate, sulfate, and molybdate minerals. For metals whose solubility is limited by carbonate minerals (e.g., Zn, Cu), dissolved concentrations can only increase if pH or HCO_3^- concentrations decrease. No clear trend in this direction is apparent from the past 10 years of water quality monitoring. Some acid mine drainage does exist within the boundaries of the Continental Pit, and it is possible that the volume and/or severity of this AMD could increase in the future with continued weathering of the ore body. This scenario cannot be evaluated at the present time.

Other significant findings from this study include the following:

- The Sarsfield Well has a lower pH when freshly sampled compared to when the water has been allowed to sit in the open for several minutes. This is probably due to degassing of dissolved CO_2 .

- The isotopic composition of water in the Sarsfield Well shows no evidence that the Berkeley Pit or tailings pond is currently leaking water to the Continental Pit.
- Based on S-isotopes, sulfate in the Sarsfield Well, as well as the acidic Pavilion Seep, is most likely derived from oxidation of pyrite and other sulfide minerals on the mine walls.
- The $\delta^{13}\text{C}$ of dissolved inorganic carbon in the Sarsfield Well is quite a bit heavier than DIC from the flooded mine shafts of Butte. Some of this difference could be due to the relative amounts of calcite and rhodochrosite in the district, as previous work has shown that hydrothermal calcite contains heavier carbon compared to rhodochrosite.

Some recommendations for further work include the following:

- It is important to continue to monitor the water quality of the dewatering well and surface waters in the Continental Pit, to see if conditions change with continued mining and with continued weathering of the mine walls.
- Modeling these data in a program such as PHREEQC could give more information about the water quality of a hypothetical Continental Pit lake, including changes in water chemistry that might occur over time in response to changes in the relative volumes of Sarsfield-like water and Pavilion-like water.
- Measuring the isotopic composition of calcite in the Continental Pit might help answer the question of whether the DIC of the Sarsfield Well is isotopically heavy due to mineral-buffering, or due to loss of CO_2 during sampling.
- Measuring the isotopic composition of water in the Sarsfield Well could be a low-cost method to test if leakage from the Berkeley Pit or tailings pond into the expanding Continental Pit occurs in the future.

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